

**BEST AVAILABLE COPY**  
REMARKS

Claims 11-18 and 20 are pending in the present application.

At the outset, Applicants wish to thank Examiner Teskin for the indication that the rejection over Arai et al has been withdrawn (paper number 14, page 2, paragraph 2). In addition, Applicants wish to thank the Examiner for pointing out the error in un-entered Claim 20 presented in the response filed May 13, 2004. In view of the fact that this response was not entered, Applicants have corrected this error in the claims by amendment above and have designated Claim 20 as "New." Reconsideration of the remaining rejection over EP 0721954 is requested in view of the following remarks and the amendment set forth above.

The rejection of Claims 11-19 under 35 U.S.C. §103(a) over EP 0721954 is respectfully traversed.

EP 0721954 discloses a transition metal compound useful as a catalytic compound for olefin polymerization (see Abstract). According to EP 0721954, this transition compound is used in the homopolymerization of an  $\alpha$ -olefin and the copolymerization of an  $\alpha$ -olefin with another  $\alpha$ -olefin. However, at no point does EP 0721954 disclose or suggest employing their catalytic compound for the copolymerization of an  $\alpha$ -olefin and an aromatic vinyl compound or the advantages obtained thereby.

Applicants note that the  $\alpha$ -olefin-aromatic vinyl copolymerization in the presence of the alkylene/silylene bis-bridged metallocene catalyst or the alkylene/alkylene bis-bridged metallocene catalyst was not known in the art at the time of the present invention. As the Examiner concedes at page 3, last paragraph of paper number 14, aromatic vinyl compounds are chemically quite different from  $\alpha$ -olefins as the ethylenic double bond is conjugated with

a phenyl ring in the aromatic vinyl compound whereas the ethylenic double bond is isolated in  $\alpha$ -olefins such as 1-octene used in EP 0721954.

In the response filed on October 6, 2003, Applicants noted that the differences in the electronic structure would lead to a corresponding difference of copolymerizability of the aromatic vinyl compounds as compared to  $\alpha$ -olefins. In the last paragraph on page 3 of paper number 14, the Examiner disregards this assertion by Applicants noting, "there is no objective basis in the record for applicants' inference of a "corresponding difference of copolymerizability." More importantly, there is no evidentiary basis for inferring a difference in reactivity of such magnitude that one of ordinary skill would have had no reasonable expectation of copolymerizing an acyclic  $\alpha$ -olefin with an aromatic vinyl compound by practicing the preparation method of European."

In response thereto, Applicants **submit herewith** the following references:

- 1) Zambelli et al, *Macromol. Symp.* 89, 373-382 (1995), and
- 2) Ishihara, *Macromol. Symp.* 89, 553-562 (1995).

The Examiner's attention is specifically drawn to Table 1 at page 376 of Zambelli et al, which shows the difference of polymerizability of ethylene and styrene. In Table 1 of Zambelli et al, a comparison is provided of the activities of the catalyst in the polymerization of ethylene and styrene when the polymerization is performed using a new catalyst and an aged catalyst. From these data the new catalyst results in a dramatically higher activity in ethylene polymerization at 0°C compared to styrene polymerization. This result indicates that polymerizability of ethylene and styrene is quite different even when the same catalyst is used.

The Examiner is also directed to Table 2 at page 561 of Ishihara, which shows the difference of polymerizability of propylene and styrene. This table shows the relationships

between the catalyst and stereoregularity of propylene polymer and styrene polymer. This result indicates that the two different stereoregular polymers have been obtained by using the same catalyst.

In view of the foregoing, it is clear that the skilled artisan would appreciate that the polymerizability of ethylene and styrene is different. More importantly, the skilled artisan would recognize that the differences in the electronic structure would lead to a corresponding difference of copolymerizability of the aromatic vinyl compounds as compared to  $\alpha$ -olefins.

Moreover, Applicants note that EP 0721954 merely lists several vinyl compounds together with  $\alpha$ -olefins and does not actually teach or describe that the aromatic vinyl compounds act as co-monomer equally to the exemplified  $\alpha$ -olefin such as 1-octene. In view of the art recognized differences in chemical properties, there can be no reasonable basis for the artisan to conclude and/or expect based on this disclosure that there would be a reasonable expectation of success in view of the disclosure of EP 0721954. Further, in view of these chemical differences, it would not be obvious to the skilled artisan to expect that the catalyst of EP 0721954 used in the olefin-olefin copolymerization is equally applicable to the claimed method, i.e., an  $\alpha$ -olefin-aromatic vinyl copolymerization.

Accordingly, EP 0721954 provides no reasonable basis to arrive at the present invention absent Applicants' disclosure.

In regard to new Claim 20, both  $Y^1$  and  $Y^2$  are limited to the alkylene groups and the substituent groups based on the description at page 6, penultimate line to page 7, line 5 of the originally filed specification.

It is evident from Examples 1-3 and 6 and Examples 4-5 and 7 that the alkylene/alkylene bis-bridged catalyst exhibits high copolymerization activity as compared to the alkylene/silylene bis-bridged catalyst. At page 7, third paragraph of paper number 14, the

Examiner asserts that Examples 1-3 and 6 and Examples 4-5 and 7 are not side-by-side comparative tests. In addition, the Examiner asserts that the catalysts of Examples 4-5 and 7 contain indenyl ligands substituted at 3-position with n-butyl or trimethylsilyl, whereas the catalysts of Examples 1-3 and 6 contain unsubstituted indenyl groups. However, Applicants submit that the catalysts with ligands having a bulky substituent group as used in the Example 4-5 and 7, would exhibit practically lower copolymerization activity as compared to the catalyst not having such bulky ligands, due to steric hindrance. However, the catalysts of Examples 4-5 and 7 exhibit unexpectedly high copolymerization activity as compared to the catalysts of Examples 1-3 and 6.

EP 0721954 merely recites the alkylene /alkylene bis-bridged catalysts and the alkylene/silylene bis-bridged catalysts and teaches that these catalysts are equivalent. In addition, at no point does EP 0721954 disclose or suggest that the alkylene/alkylene bis-bridged catalysts exhibit high copolymerization activity as compared to the alkylene/silylene bis-bridged catalyst and also fails to actually teach the alkylene/alkylene bis-bridged catalysts in its working examples.

Not only is EP 0721954 silent with respect to the claimed  $Y^1$  and  $Y^2$  groups of Claim 20, Applicants further submit that the scope of experimental evidence is commensurate with the degree of protection sought by the claim. Therefore, Applicants submit that new Claim 20 should be allowable over EP 0721954.

Applicants request withdrawal of the rejection over EP 0721954.

Applicants submit that the present application is in condition for allowance. Early notification to this effect is respectfully requested.

Respectfully submitted,

OBLON, SPIVAK, McCLELLAND,  
MAIER & NEUSTADT, P.C.  
Norman F. Oblon



Vincent K. Shier, Ph.D.  
Registration No. 50,552

Customer Number

**22850**

Tel: (703) 413-3000

Fax: (703) 413-2220

(OSMMN 08/03)

NFO/VKS

**FULL TEXT OF CASES (USPQ2D)**  
All Other Cases

**In re Dow Chemical Co. (CA FC) 5 USPQ2d 1529 In re Dow Chemical Co.**

**U.S. Court of Appeals Federal Circuit**  
**5 USPQ2d 1529**

**Decided January 25, 1988**  
**No. 87-1406**

**Headnotes**

**PATENTS**

**1. Patentability/validity -- Obviousness -- Evidence of (§ 115.0903)**

**Patentability/validity -- Obviousness -- Secondary considerations (§ 115.0907)**

Board of Patent Appeals and Interferences erred in rejecting as obvious claims for invention of impact resistant rubber-based resin suitable for molding and extrusion containing preferred ingredients styrene, maleic anhydride, and synthetic diene rubbers, since none of prior art references cited by patent holder and PTO suggest that any process could be used successfully in such three-component system to produce resin having desired properties, and since board did not give fair evidentiary weight to expert's skepticism concerning invention, or to five to six years necessary to produce invention, in determining obviousness issue.

**Particular Patents -- Chemical -- Rubber Based Resins**

3,919,354, Moore, Lehrer, Lyons and McKeever, impact resistant polymers of a resinous copolymer of an alkenyl aromatic monomer and unsaturated dicarboxylic anhydride, holding of obviousness reversed.

**Case History and Disposition:**

Page 1529

**Appeal from the U.S. Patent and Trademark Office Board of Patent Appeals and Interferences.**

**Reexamination of Patent No. 3,919,354, held by The Dow Chemical Company. From decisions rejecting all claims of patent as obvious, patent holder appeals. Reversed.**

**Attorneys:**

**Douglas N. Deline, Midland, Mich. (Berndt W. Sandt with him on the brief) for appellant.**

**John H. Raubitschek, associate solicitor, Arlington, Va. (Joseph F. Nakamura, solicitor, and Fred E. McKelvey, deputy solicitor, with him on the brief) for appellee.**

**Judge:**

**Before Smith, Nies, and Newman, Circuit Judges.**

**Opinion Text****Opinion By:**

**Newman, Circuit Judge.**

Dow Chemical Company appeals the decisions of the United States Patent and Trademark Office Board of Patent Appeals and Interferences, No. 86-3426 (Feb. 25, 1987) and No. 662-81 (Mar. 25, 1986), together rejecting all the claims on reexamination of United States Patent No. 3,919,354 entitled "Impact Resistant Polymers of a Resinous Copolymer of an Alkenyl Aromatic Monomer and an Unsaturated Dicarboxylic Anhydride.". We reverse.

***The Rejection***

The invention is an impact resistant rubber-based resin having improved resistance to heat distortion. Claim 28, the broadest claim on appeal, is illustrative:

28. A polymer suitable for molding and extrusion, of substantially improved resistance to mechanical shock and impact, the polymer consisting essentially of the polymerization product of

a. a monovinyl alkenyl aromatic monomer containing up to 12 carbon atoms and having the alkenyl group attached directly to the benzene nucleus, the al

Page 1530

kenyl aromatic compound being present in a proportion of from about 65 to 95 parts by weight and from 35 to 5 parts by weight of an unsaturated dicarboxylic acid anhydride readily copolymerizable therewith, and

b. from 5 to 35 parts by weight of a diene rubber per 100 parts of (a) plus (b), the rubber consisting essentially of 65 to 100 weight percent butadiene, or isoprene and up to 35 weight percent of an alkenyl aromatic hydrocarbon as the sole other monomer in the rubber, the rubber having a glass temperature not higher than 0° C., the rubber being in the form of a plurality of particles having diameters within the range of 0.02 to 30 microns dispersed throughout a matrix of polymer of alkenyl aromatic monomer and the anhydride, at least a major portion of the rubber particles containing distinct occlusions of the polymer of (a), with the further limitation that the polymer of (a) is a nonequimolar random copolymer.

The preferred ingredients are styrene, maleic anhydride, and synthetic diene rubbers, and our discussion will be in these terms, as was the Board's.

The Board's decision that the claimed invention would have been obvious in terms of 35 U.S.C. §103 was based on the combination of two references: a 1966 article by Molau and Keskkula entitled "Heterogeneous Polymer Systems IV. Mechanism of Rubber Particle Formation in Rubber-Modified Vinyl Polymers", and Baer U.S. Patent No. 2,971,939. Also discussed were Farmer U.S. Patent No. 2,275,951 and a publication by Bacon and Farmer entitled "The Interaction of Maleic Anhydride with Rubber", although the Board stated that the rejection was sustainable without relying on either of these references.

### ***The Prior Art***

The Molau/Keskkula article shows the preparation of a resin having high impact strength by dissolving synthetic diene rubber in styrene and polymerizing the styrene. This reference teaches that phase inversion is necessary to the formation of these moldable, extrudable resins. Baer prepares nonequimolar random maleic anhydride-styrene copolymers by a technique whose salient feature is adding the maleic anhydride slowly to polymerizing styrene under controlled conditions.

Farmer shows the reaction among natural rubber, styrene, and maleic anhydride, and also states that maleic anhydride reacts directly with the rubber. The Bacon and Farmer article also shows the reaction of maleic anhydride with natural rubber. These products, according to Dow's evidence and as found by the Board, do not have a dispersed rubber phase containing occlusions, and are not moldable.

Dow argues that the Board has engaged in hindsight reconstruction of the claimed invention. To support its position Dow refers to several scientific publications and other references, in addition to those cited by the PTO, and evidence submitted by declaration and deposition.

The first group of references to which Dow refers shows the reaction of maleic anhydride with natural or synthetic rubbers. These references show both intermolecular and intramolecular reactions between maleic anhydride and the various rubbers, but not a grafted rubber, which is said by Dow to characterize its product. Additional references are cited by Dow to show that maleic anhydride is much more reactive with diene-type synthetic rubbers than with natural rubber, and that the reaction with the synthetic rubbers is difficult to control and the product is unpredictable. Another reference cited by Dow, the *Encyclopedia of Science and Technology*, states the general rule, derived from experience with acrylonitrile, that copolymers with synthetic diene rubbers have elevated glass transition temperatures; Dow advises that this is a highly undesirable property for a high-impact strength resin.

Another series of references cited by Dow shows several known techniques of reacting styrene and maleic anhydride to prepare nonequimolar copolymers, all different from the technique shown in the Baer patent.

### ***Analysis***

The Board held that the claimed product results from the application of the Baer technique to a styrene-maleic anhydride polymer system which includes synthetic diene rubber, and that it would have been obvious to do that which these inventors did if one wanted to increase the heat stability of a known high impact styrene rubber resin. The crux of Dow's argument is that no reference shows or suggests that these references should or could be combined successfully. Indeed, the Board agreed, stating that "[i]t is not apparent from the evidence whether rubber and maleic anhydride would have been expected to react *in the process suggested by the combined disclosure of Molau and*



*Baer . . . .*" (Emphasis in original).

Page 1531

Dow also points out, referring to the Keskkula evidence, that it was believed that these products could not be made by the mass polymerization techniques of the prior art. Dow asserts that no reference, including Baer, suggested that the Baer technique could produce the requisite phase inversion in a system containing diene rubber, and could produce a diene-rubber containing resin that could be molded and had the other desired high-impact and thermal properties.

Dow refers to the Farmer patent, cited by the examiner and the Board, which shows that the reaction of styrene, maleic anhydride, and natural rubber forms a product that is unsuitable as a molding resin. Dow argues that Farmer leads away from the Dow invention, in that Farmer obtains precisely the "runaway" reaction, and undesirable product, that Keskkula believed was characteristic of reactions involving styrene, maleic anhydride, and rubbers. Dow points to Dr. Keskkula's Report to Dow management, written in 1966 at about the time the present invention was made, pointing out the many problems in attempting to produce the three-component product that these inventors later succeeded in producing.

In response, the Commissioner argues that even though an expert polymer scientist, Dr. Keskkula, "personally may have been surprised by the invention at the time it was made, it does not necessarily follow that the invention would have been unobvious to one of ordinary skill in the art." The Commissioner suggests that one less encumbered by knowledge of the need for phase inversion, as described in the Molau/Keskkula article, might have achieved the Dow product by combining the references in the way suggested by the Commissioner. Reflecting on this theory of invention, we observe that such a person did not do so, despite the decades of experimentation with these components, and the recognition of need, as evidenced by the many references cited by both sides. *See In re Geiger*, 815 F.2d 686, 688, 2 USPQ2d 1276, 1278 (Fed. Cir. 1987); *ACS Hospital Systems, Inc. v. Montefiore Hospital*, 732 F.2d 1572, 1577, 221 USPQ 929, 933 (Fed. Cir. 1984).

The Board held that Dow's statement in the patent specification that it was known that styrene/maleic anhydride copolymers had improved heat resistance as compared with styrene rubbers, made it *prima facie* obvious to combine these three components. Indeed, the record shows that such combinations had previously been made, in various ways, but without producing the product here desired. That there were other attempts, and various combinations and procedures tried in the past, does not render obvious the later successful one. The PTO's reliance on Dow's "admission" of longfelt need as *prima facie* evidence of obviousness is contrary to logic as well as law. Recognition of need, and difficulties encountered by those skilled in the field, are classical indicia of unobviousness. *Graham v. John Deere Co.*, 383 U.S. 1, 17, 148 USPQ 459, 467 (1966); *Custom Accessories v. Jeffrey-Allan Industries*, 807 F.2d 955, 960, 1 USPQ2d 1196, 1199 (Fed. Cir. 1986). Further, a patent applicant's statement of the purpose of the work is not prior art.

The Board thus concluded that although one would not know in advance whether the Baer technique would work at all in the presence of diene rubber, or produce a moldable high-impact product, if it did succeed it would have been obvious. The Board criticized Keskkula's evidence for not stating whether, after these inventors proposed the procedure here at issue, Keskkula would have expected the maleic anhydride to react preferentially with the diene rubber or with the styrene and to what effect on the impact properties of the product. The PTO argues that unless the prior art is shown to have led one of ordinary skill to expect the Baer technique to fail, the applicant's burden is not met. This is not the criterion. That these inventors eventually succeeded when they and others had failed does not mean that they or their colleagues must have expected each new idea to fail. Most technological advance is the fruit of methodical, persistent investigation, as is recognized in 35 U.S.C. §103 ("Patentability shall not be negated by the manner in which the invention was made").

The consistent criterion for determination of obviousness is whether the prior art would have suggested to one of

ordinary skill in the art that this process should be carried out and would have a reasonable likelihood of success, viewed in the light of the prior art. See *Burlington Industries v. Quigg*, 822 F.2d 1581, 1583, 3 USPQ2d 1436, 1438 (Fed. Cir. 1987); *In re Hedges*, 783 F.2d 1038, 1041, 228 USPQ 685, 687 (Fed. Cir. 1987); *Orthopedic Equipment Co. v. United States*, 702 F.2d 1005, 1013, 217 USPQ 193, 200 (Fed. Cir. 1983); *In re Rinehart*, 531 F.2d 1048, 1053-54, 189 USPQ 143, 148 (CCPA 1976). Both the suggestion and the expectation of success must be founded in the prior art, not in the applicant's disclosure.

In determining whether such a suggestion can fairly be gleaned from the prior art, the full field of the invention must be considered; for the person of ordinary skill is charged

Page 1532

with knowledge of the entire body of technological literature, including that which might lead away from the claimed invention. The Commissioner argues that since the PTO is no longer relying on Farmer or the Bacon and Farmer article, the applicant is creating a "straw man". It is indeed pertinent that these references teach against the present invention. Evidence that supports, rather than negates, patentability must be fairly considered.

[1] The PTO presents, in essence, an "obvious to experiment" standard for obviousness. However, selective hindsight is no more applicable to the design of experiments than it is to the combination of prior art teachings. There must be a reason or suggestion in the art for selecting the procedure used, other than the knowledge learned from the applicant's disclosure. *Interconnect Planning Corporation v. Feil*, 774 F.2d 1132, 1143, 227 USPQ 543, 551 (Fed. Cir. 1985). Of the many scientific publications cited by both Dow and the PTO, none suggests that any process could be used successfully in this three-component system, to produce this product having the desired properties. The skepticism of an expert, expressed before these inventors proved him wrong, is entitled to fair evidentiary weight, see *In re Piasecki*, 745 F.2d 1468, 1475, 223 USPQ 785, 790 (Fed. Cir. 1984); *In re Zeidler*, 682 F.2d 961, 966, 215 USPQ 490, 494 (CCPA 1982), as are the five to six years of research that preceded the claimed invention. The evidence as a whole does not support the PTO's conclusion that the claimed invention would have been obvious in terms of 35 U.S.C. §103.

**REVERSED**

**- End of Case -**



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**89**

Macromol. Symp.  
Vol. 89, January 1995

MSYMEC  
Vol. 89, 1-586

Hüthig & Wepf Verlag  
Zug, Heidelberg, Oxford, CT/USA

## MECHANISM OF SYNDIOTACTIC-SPECIFIC POLYMERIZATION OF STYRENE†

Adolfo Zambelli\*, Claudio Pellecchia and Antonio Proto

Dipartimento di Fisica, Università di Salerno, I-84081 Baronissi (SA), Italy

**Abstract:** Perusal of literature data and some new results concerning syndiotactic-specific polymerization of styrene suggest a reaction mechanism accounting for the steric control. Key features of the proposed mechanism are stereorigid  $\eta^5$  coordination of the growing chain end and diastereoselective coordination of the monomer imposed by direct interactions with the ancillary ligand of the metal complex, a pseudotetrahedral chiral Ti(III) or Zr(III) cation, which inverts its configuration after every syndiospecific insertion step.

### INTRODUCTION

In 1986 Ishihara discovered that a variety of hydrocarbon soluble titanium compounds, in the presence of methylaluminoxane (MAO), promote syndiotactic specific polymerization of styrene and substituted styrenes (Ref. 1).

Very active catalysts are obtained by using as catalyst precursors half-titanocenes (Ref. 1), like  $CpTiX_3$  or  $CpTiX_2$ , ( $Cp$  = cyclopentadienyl,  $X$  = halide or hydrocarbyl) while titanocenes ( $Cp_2TiX_2$  or  $Cp_2TiX$ ) afford very poorly active catalysts. (Refs. 2, 3)

Syndiotactic specific polymerization of styrene can be also promoted by using, in proper conditions, zirconium instead of titanium compounds but the activity and the stereoregularity of the resulting polystyrenes are lower (Refs. 4-6). On this subject, it is worth noting that half-zirconocenes, such as  $CpZrCl_3$  and  $CpZrBz_3$  ( $Bz$  = benzyl), are practically ineffective in the usual reaction conditions (Ref. 6, 7).

In this paper, on the basis of a critical review of some experimental data concerning this polymerization, we propose a reaction mechanism accounting for the steric control, at least in the presence of catalysts based on half-titanocenes.

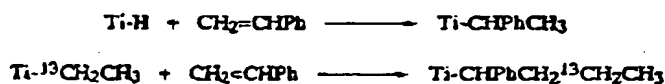
† This paper is dedicated to the memory of Professor Mario Farina.

## RESULTS AND DISCUSSION

## 1) Regiospecific insertion

$^{13}\text{C}$  NMR analysis of syndiotactic polystyrene, obtained in the presence of  $\text{Ti}(\text{CH}_2\text{Ph})_4$  - MAO at  $50^\circ\text{C}$ , showed the end groups  $\cdots\text{CHPhCH}_3$  and  $\text{PhCH}=\text{CH}\cdots$  in equal amounts (Ref. 8). When the polymerization was performed by adding  $\text{Al}(^{13}\text{CH}_2\text{CH}_3)_3$  to the same catalytic system,  $\cdots\text{CHPhCH}_2^{13}\text{CH}_2\text{CH}_3$  end groups were also detected (Ref. 9). No evidence of regioirregularly arranged monomer units is found by  $^{13}\text{C}$  NMR analysis (Ref. 8).

The polymer chains can thus start both from Ti-H and Ti- $^{13}\text{CH}_2\text{CH}_3$  bonds and the insertion of the monomer is always secondary:



The unsaturated end groups obviously arise from  $\beta$ -hydrogen abstraction:



or possibly from chain transfer with the monomer.

Another chain transfer process can involve aluminum alkyls, e. g.  $\text{Al}(\text{CH}_3)_3$ , according to the scheme:



Analogous results are obtained in the presence of  $\text{CpTiCl}_3$  - MAO.

It is worth mentioning that secondary insertion of the monomer was previously observed for syndiotactic-specific polymerization of propene in the presence of  $\text{VCl}_4\text{-AlR}_2\text{Cl}$  (Ref. 10). However secondary insertion of propene only results from too large non-bonded interactions occurring in case of primary insertion of the incoming monomer, with the polymer chain already bonded to V through a secondary carbon (Refs. 10-12). On the contrary, insertion of the incoming monomer on either V- $\text{CH}_2\cdots$  or V- $\text{CH}_3$  bonds, occurring during copolymerization with  $\text{C}_2\text{H}_4$  and in the initiation step when using  $\text{Al}(\text{CH}_3)_2\text{Cl}$  or  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$  or  $\text{Al}(\text{iC}_4\text{H}_9)_2\text{Cl}$  as organometallic cocatalyst, is largely primary (Refs. 12, 13).

In contrast, as previously mentioned, secondary insertion of styrene is always favoured, even on Ti-H bonds, and is related to the stronger  $\eta^\pi$  bond of the growing chain end with the transition metal, which can result only if the monomer is inserted in a secondary mode.

## 2) Addition to the double bond

$^1\text{H}$  NMR analysis of copolymers of perdeuteriostyrene with  $Z-1-d_1$ -styrene, obtained in the presence of  $\text{Ti}(\text{CH}_2\text{Ph})_4$ -MAO, allowed us to investigate the mechanism of the addition to the double bond (Ref. 14). *Cis* addition was established from the value of the coupling constant between the vicinal protons of the copolymer, following the same method previously reported for syndiotactic polypropylene (Ref. 15).

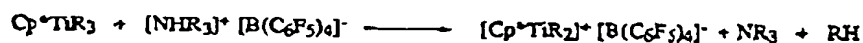
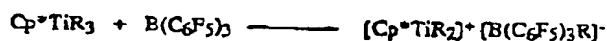
## 3) Statistical model of the stereospecific propagation

$^{13}\text{C}$  NMR analysis of syndiotactic polystyrene obtained in the presence of  $\text{Zr}(\text{CH}_2\text{Ph})_4$ -MAO shows that the statistical sequence of the stereochemical configurations of the tertiary carbons is first order Markovian (i.e. the statistical sequence of the syndiotactic (*r*) and the isotactic (*m*) dyads is Bernoullian) (Refs. 4, 16). Similar results are obtained by using as a catalyst  $\text{CpTiCl}_3$ -MAO (Ref. 17). Polystyrenes prepared in the presence of  $\text{Cp}^*\text{TiCl}_3$ -MAO ( $\text{Cp}^*$  = pentamethylcyclopentadienyl) are almost perfectly stereoregular (Ref. 17).

An attempt to evaluate the driving force of the stereospecific insertion was made by plotting  $\ln P_r / (1-P_r)$  versus  $1/T$  (where  $P_r$  is the probability of syndiotactic placements, and  $T$  = polymerization temperature) for polymers prepared at different temperatures in the presence of  $\text{Zr}(\text{CH}_2\text{Ph})_4$ -MAO (Ref. 16). A low Arrhenius coefficient  $A$  ( $A = RT \ln P_r / (1-P_r) \approx 1.5$  Kcal/mol) was found, although the polymers were very stereoregular ( $P_r$  ranges between 0.94 and 0.91 while the temperature is raised from 40 up to 120 °C).

## 4) Cationic active species

Reaction of titanium hydrocarbyls such as  $\text{Cp}^*\text{TiR}_3$  ( $R$  = hydrocarbyl) with either  $\text{B}(\text{C}_6\text{F}_5)_3$  (Ref. 7) or  $[\text{NHR}_3]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  (Ref. 18), according to the scheme:



provides efficient catalysts promoting syndiotactic specific polymerization of styrene (Refs. 7, 18). However, NMR and ESR monitoring of these reactions showed that the initially formed  $\text{Ti(IV)}$  cationic complexes stepwise decompose, possibly leading to reduced  $\text{Ti}$  species (Ref. 17). As a consequence it is not immediately apparent whether the active species are the just mentioned  $\text{Ti(IV)}$  complexes or some decomposition product, possibly a  $\text{Ti(III)}$  complex.

Chien (Ref. 19) provided evidence that the oxidation state of  $\text{Ti}$  of the active species is +3, at least when the catalyst precursor is a half-titanocene. We have recently obtained data supporting this finding (Ref. 17).

Tab. 1. Effects of catalyst ageing on the activity of  $\text{Cp}^*\text{TiCl}_3\text{-MAO}$  in the polymerization of ethylene and styrene.<sup>a)</sup>

Monomer	Ageing at 70 °C min	Polymerization T °C	Yield mg
styrene	-	0	10
styrene	20	0	291
ethylene	-	0	436
ethylene	20	0	124

a) Polymerization conditions:  $\text{Cp}^*\text{TiCl}_3 = 2.0 \cdot 10^{-5}$  mol; MAO = 0.02 mol (based on Al); toluene = 50 mL; polymerization time = 30 min; styrene = 5 mL; ethylene = 1 atm.

In Tab. 1 is reported a comparison of the activities of  $\text{Cp}^*\text{TiCl}_3\text{-MAO}$  in the polymerization of ethylene and styrene when the polymerizations are performed immediately after mixing the two catalyst components or after ageing the catalytic system. One can observe that a moderate ageing at 70 °C results in a lower activity in ethylene polymerization (at 0 °C), but in a higher activity in styrene polymerization. Prolonged ageing leads to catalyst deactivation. This finding suggests that the initially formed  $[\text{Cp}^*\text{Ti}(\text{CH}_3)_2]^+$  cation is only able to promote ethylene polymerization.

#### 5) Polymerization of other monomers and copolymerization

The same catalytic systems which promote syndiospecific polymerization of styrene are also active in the polymerization of ethylene and  $\alpha$ -olefins (Refs. 20, 21), substituted styrenes (Ref. 1) and conjugated diolefins (Refs. 22, 23). These monomers can be also copolymerized to each other (Refs. 24-26).

The most interesting information is:

- Substituted styrenes afford syndiotactic polymers and, of course, copolymerize with styrene. The copolymers are co-syndiotactic and the polymerization rate increases while increasing the nucleophilicity of the monomer (Refs. 1, 24).
- 1,3-Butadiene and isoprene afford *cis*-1,4 polymers. 4-Methyl-1,3-pentadiene affords a 1,2-syndiotactic polymer (Ref. 22).
- At low temperature *Z*-1,3-pentadiene affords a 1,2-syndiotactic polymer, while a *cis*-1,4 polymer is produced at higher temperatures (Ref. 23).
- The reactivity of 4-methyl-1,3-pentadiene is particularly high, both in comparison with styrene and 1,3-butadiene (Refs. 22, 25).
- 1,3-butadiene and isoprene copolymerize to each other and with styrene (Ref. 24). The reactivity ratios in copolymerizations are not generally equal to the ratios of the corresponding homopolymerization rates (Ref. 25).



According to the literature, the many results briefly summarized above seem to show that the electrophilic attack of the monomer by a nucleophile is rate determining the incorporation, and that the insertion of the coordinated monomer into the M-C bond is affected by the nature of the last unit of the growing chain end (Ref. 25). The whole picture is in good agreement with the hypothesis that the active species are organometallic cations, the very ones mentioned in section 4 for the polymerization of olefins, and, most likely, the M(III) analogues resulting from reductive decomposition for the polymerization of styrene and conjugated diolefins.

According to Porri and coworkers (Ref. 23), 1,2-syndiotactic polymerization of Z-1,3-pentadiene suggests an  $\eta^2$  coordination of the incoming monomer to the transition metal, followed by fast 2,1 (secondary) syndiotactic-specific insertion. At higher temperatures, fast  $\eta^2 \rightarrow \eta^4$  isomerization of the coordinated Z-1,3-pentadiene could occur and, subsequently, *cis*-1,4 insertion, with lower rate, would result. Reasonably,  $\eta^4$  coordination could be hardly possible for both 4-methyl-1,3-pentadiene and styrene, and consequently  $\eta^2$  coordination would be always involved in syndiotactic polymerization of both these monomers.

#### 6) Activity of different catalysts

As mentioned in the introduction, the activity of the different catalysts in promoting polymerization of styrene is strongly dependent on the transition metal precursor.

In the presence of MAO the activity of the titanium-based catalysts decreases while changing the precursor in the following order (Refs. 1-6):



According to Chien, (Ref. 27) catalysts prepared from half-titanocenes are especially active due to both a larger amount of active species and to a higher propagation rate constant. Zr catalysts are usually less active, and, in particular, it is noteworthy that half-zirconocenes are very little active (Refs. 6, 7).

Obtaining different concentrations of active species when allowing to react MAO with different precursors is not surprising at all.

The different propagation rate constants could be explained, e. g., by considering the possibility of different ancillary ligands on the active species affecting the electrophilicity and possibly the

intimate ion pair  $\rightleftharpoons$  free ions

equilibrium, if one assumes that the free cation may efficiently promote the propagation.

The high activity of the  $\text{CpTiX}_3$ -MAO catalysts, as opposed to the negligible activity of the  $\text{CpZrX}_3$ -MAO ones, might be due, at least in part, to the higher stability of Zr(IV) in comparison with Ti(IV) (Ref. 28).

## 7) Model compounds

Several Zr cations, bearing benzyl ligands and, possibly, other ancillary ligands have been isolated and characterized by NMR and X-Ray diffraction analysis (Refs. 29-33) (see Fig. 1).

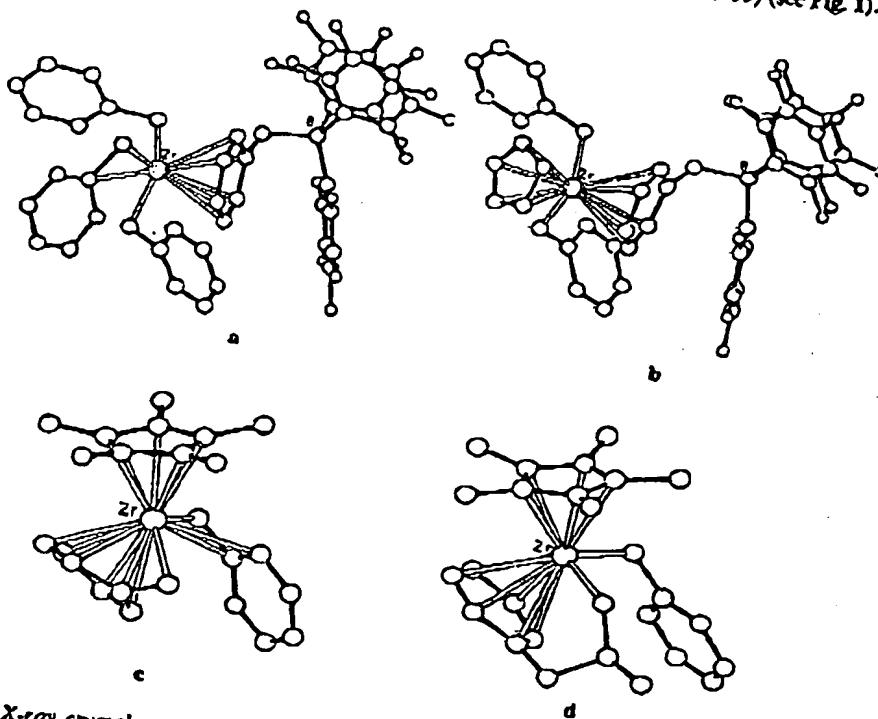


Fig. 1. X-ray crystal structures of  $[Zr^+](CH_2Ph)_3(\eta^6-PhCH_2B^-(C_6F_5)_3)$  (a) (Ref. 30);  $[Cp^*Zr^+](CH_2Ph)_2(\eta^5-PhCH_2B^-(C_6F_5)_3)$  (b) (Ref. 31);  $[Cp^*Zr(\eta^1:\eta^6-CH_2CHMeCH_2Ph)(CH_2Ph)]^+$  (c) (Ref. 32);  $[Cp^*Zr(\eta^1:\eta^6-CH_2CHMeCH_2Ph)(CH_2Ph)]^+$  (d) (Ref. 33). In the case of c and d, the  $[B(CH_2Ph)(C_6F_5)_3]^-$  anions are not in the coordination sphere of Zr.

Benzyl ligands were chosen because they are closely related to the growing chain end resulting from secondary insertion of styrene (Refs. 8, 9). Common features of these complexes are the distorted pseudotetrahedral coordination geometry around Zr, and the relieving of the electronic unsaturation of the cation either by arene coordination of the benzyl ligand of the counterion to give a zwitterion (as in a and b), or by  $\eta^n$  ( $n > 1$ ) coordination of some benzyl ligand (as in a and c), or even by chelating  $\eta^1:\eta^6$  coordination of the (2-methyl)(3-phenyl)propyl ligand (as in d).

None of the above complexes appreciably promotes syndiotactic-specific polymerization of styrene in the usual reaction conditions, and simple inspection of Fig. 1 suggests that this might be due to steric overcrowding making the coordination of styrene hardly possible.

#### 8) Stereochemical reaction mechanism

At the present, in view of the experimental findings reviewed in the previous sections, our belief concerning the reaction mechanism, at least in the presence of catalytic systems based on half-metallocenes, is that the active species are group 4 metal cations with oxidation state +3.

E. g., removing the  $\eta^3$  benzyl from the chiral Zr(IV) complex  $[\text{Cp}^*\text{Zr}(\eta^3\text{-CH}_2\text{Ph})(\eta^7\text{-CH}_2\text{Ph})]^+$  (see Fig. 1c) (Ref. 32),  $\eta^2$  coordination of styrene becomes possible to give the diastereomeric intermediate 17-electron Zr(III) cation  $[\text{Cp}^*\text{Zr}(\eta^7\text{-CH}_2\text{Ph})(\eta^2\text{-CH}_2=\text{CHPh})]^+$ . In Fig 2A is reported the possible molecular structure of such a cation with an  $\alpha$  substituted  $\eta^7$  benzyl resembling the growing polymer chain.

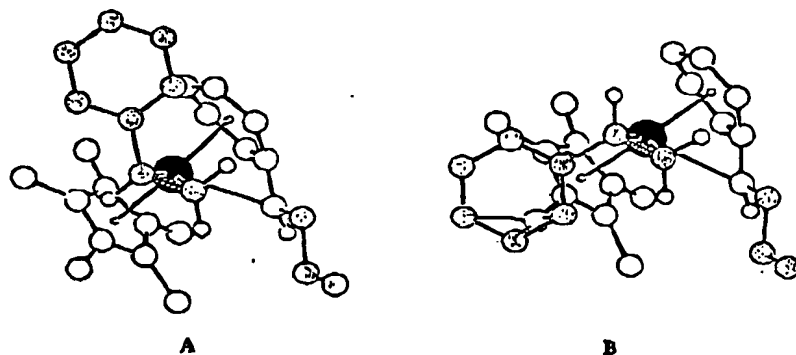


Figure 2. Molecular models of the diastereomeric intermediate cations  $[\text{Cp}^*\text{Zr}(\eta^7\text{-CH}_2\text{Ph})(\eta^2\text{-CH}_2=\text{CHPh})]^+$ . The above models have been obtained from the crystal structure of  $[\text{Cp}^*\text{Zr}(\eta^7\text{-CH}_2\text{Ph})(\eta^3\text{-CH}_2\text{Ph})]^+$  (see Fig. 1c), by replacing the  $\eta^3\text{-CH}_2\text{Ph}$  ligand with an  $\eta^2\text{-CH}_2=\text{CHPh}$  ligand arranged in a conformation suitable for *cis* ligand migration and secondary insertion (i. e. with the double bond parallel to the Zr-CHR bond and the methylene facing the methine of the last unit of the chain). The Zr-C distances for the  $\eta^2$  styrene ligand have been fixed at 2.6 Å, a value similar to those observed in Zr(IV) arene  $\pi$  complexes. The other parameters are those obtained from X-ray analysis of c (Ref. 32): Zr-Cp\* (centroid) = 2.22 Å; Zr-Ph (centroid) = 2.12 Å; Zr-CHR = 2.65 Å; Cp\* (centroid) - Zr - Ph (centroid) = 193°.

It is worth observing that coordination of the mirror related styrene enantiomer to give the diastereoisomer of Fig. 2B is hardly possible, due to the exceedingly high interactions with Cp\*, occurring when the conformation is that required by *cis* ligand migration and secondary

insertion. Considerable non-bonded interactions would also occur if the ancillary ligand were Cp instead of Cp\*.

Incorporation, by *cis* addition, of the  $\eta^2$  coordinated styrene would stepwise lead to (1)  $\eta^7$  bonding of the latter and (2) dissociation of the phenyl of the penultimate monomer unit, thus providing (3) the possibility of enantioselective  $\eta^2$  coordination of another styrene molecule to give the mirror related active species (see Fig. 3).

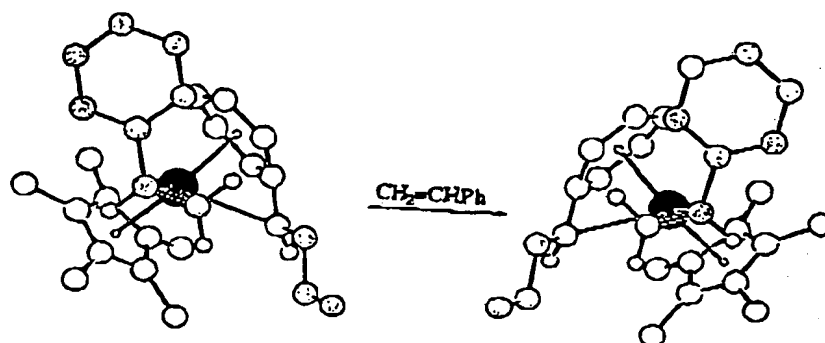


Fig. 3. Inversion of configuration of the catalytic complex after incorporation of the coordinated styrene molecule,  $\eta^7$  coordination of the growing chain end and  $\eta^2$  coordination of another styrene molecule.

According to the present view, incorporation of the monomer is at the same time a chain migratory insertion and a nucleophilic substitution at the cationic metal center by the phenyl substituent of the incoming monomer while the last unit of the growing chain is leaving. Moreover, each syndiotactic incorporation of a monomer molecule involves the inversion of configuration of the metal, while isotactic incorporation does not, thus providing a simple explanation of the statistical model of the stereospecific propagation.

Such a stereochemical reaction mechanism implies steric control of monomer incorporation by the chirality of the metal, which, in turn, is related to the configuration and conformation of the last unit of the growing chain end.

The possibility of obtaining syndiotactic-specific catalysts by using a variety of transition metal precursors even without any Cp ligand could be understood by considering that while a pseudotetrahedral coordination geometry of the transition metal is a key feature of the proposed model of the syndiotactic-specific species, there is no particular need of a Cp\* or Cp ligand. Any other bulky enough ancillary ligand could play the same role. In addition, the last unit of the growing chain end does not need to be necessarily  $\eta^7$  coordinated but any  $\eta^n$  coordination with  $n \geq 3$  might be acceptable, provided that an adequately stereorigid conformation is achieved. This is obviously the case of 2,1-syndiotactic chains arising from 4-methyl-1,3-pentadiene, and Z-1,3-pentadiene, which at most can be  $\eta^3$  coordinated.

## ACKNOWLEDGEMENTS

This work was supported by the Italian Ministry of University (MURST) and by the National Research Council (CNR), *Progetto Finalizzato Chimica Fine*.

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## SYNTHESES AND PROPERTIES OF SYNDIOTACTIC POLYSTYRENE

N. ISHIHARA

Central Research Laboratories, IDEMITSU KOSAN Co., Ltd., 1280 Karai-Izumit  
Sodegaura, Chiba 299-02, Japan

## ABSTRACT

Syndiotactic polystyrene (SPS) is a new crystalline engineering thermoplastic. With a melting point of 270 °C and its crystalline nature, SPS has high heat resistance, excellent chemical resistance and water/steam resistance. Since SPS has excellent dielectric properties, it is useful as a capacitor insulation material. The rate of crystallization is very fast in comparison with isotactic polystyrene (IPS), thus, SPS can be used in a number of forming operations, including injection molding, extrusion and thermoforming.

A system composed of a homogeneous titanium compound and methylaluminoxane (MAO) is an effective catalyst for syndiospecific polymerization of styrene. On the other hand heterogeneous titanium compounds containing halogen make a mixture of isotactic and syndiotactic components. The amount of syndiotactic polystyrene obtained is dependent on the mole ratio of Al to Ti. The result of ESR measurement suggests the  $Ti^{3+}$  species are important as a highly active site for producing syndiotactic polystyrene.

A comparison of the stereoregularities of polypropylene and polystyrene formed by various metallocene catalysts is studied. The  $(C_6H_5)_2C(η_5-C_5H_4)(η_5-C_9H_6)TiCl_2$  / MAO system gives a homogeneous catalyst for the polymerization of propylene giving isotactic rich polypropylene and of styrene to give syndiotactic polystyrene.

## INTRODUCTION

The control of stereoregularity is practically important both in the development of new polymers or tailor-made polymers and in the control of polymer properties. For polystyrene, three kinds of order can be assumed according to the orientation of the phenyl-ring relative to the polymer chain backbone as shown in Table 1: atactic, isotactic and syndiotactic. Since the discovery of Ziegler-Natta catalysis, extensive research concerning the stereospecific polymerization of olefins has been carried out. In most cases, isotactic polymers are obtained and syndiotactic polymers are rare. However, we have succeeded in synthesizing highly syndiotactic polystyrene in 1985.<sup>1,2)</sup>

## RESULTS AND DISCUSSION

### Properties of SPS

#### (1) Neat SPS

As Fig. 1 shows, polystyrenes can be classified according to their stereoregular arrangements into three forms of polymers; atactic, isotactic and syndiotactic polystyrenes. The atactic polymer is amorphous and has been manufactured commercially for over fifty years as general - purpose polystyrene. In contrast to this is a crystalline isotactic polymer synthesized with the aid of a Ziegler-Natta catalyst, and is well known for its high melting point of approximately 240 °C. This polymer is not commercially viable, however, because of its impractically low crystallization rate. On the other hand the syndiotactic polymer had been supposed to be crystalline because of its regular structure, albeit the method of synthesis was not known until recently. However, the recent advances in catalytic technology, as represented by metallocene catalysts, have drastically altered these circumstances. The development of the totally new catalysts, which made the synthesis of new polymers possible, enabled IDEMITSU to successfully synthesize the world's first syndiotactic polystyrene in 1985. The distinguishing features of the resulting polymer are a higher melting point than the isotactic polymer. It is therefore recognized as a promising crystalline thermoplastic material to be used in engineering applications. Syndiotactic polystyrene will be called SPS hereinafter.

Fig. 1 compares the typical properties of neat SPS with those of GPPS and other crystalline engineering resins. A comparison of SPS with conventional polystyrene reveals a similar glass transition temperature, but an entirely different and higher melting point of 270 °C, which can only be observed in crystalline polymers.

SPS is also highly resistant to most chemicals with the exception of some organic solvents such as aromatic hydrocarbons, which cause it to swell at room temperature.

Because SPS is a pure styrene polymer, many of its properties except for resistance to high temperature and solvents, resemble those of other well-known styrene polymers. For example, low density, high modulus of elasticity, low moisture absorbance and excellent properties at elevated temperatures. The disadvantage of being a styrene polymer is, however, its brittleness.

#### (2) Reinforced SPS

SPS, when used alone, is not suitable for structural material because of the brittleness. Reinforcing the resin with fiber-glass, mineral fillers, or elastomers is one approach to offset this. The resultant injection-mouldable composite offers properties far superior to those of existing engineering thermoplastics.

Fiberglass-reinforced SPS is as good as or better than other conventional engineering thermoplastics both in dynamic- and thermo-mechanical properties such as



Figure 1. Atactic, Isotactic and Syndiotactic Polystyrene

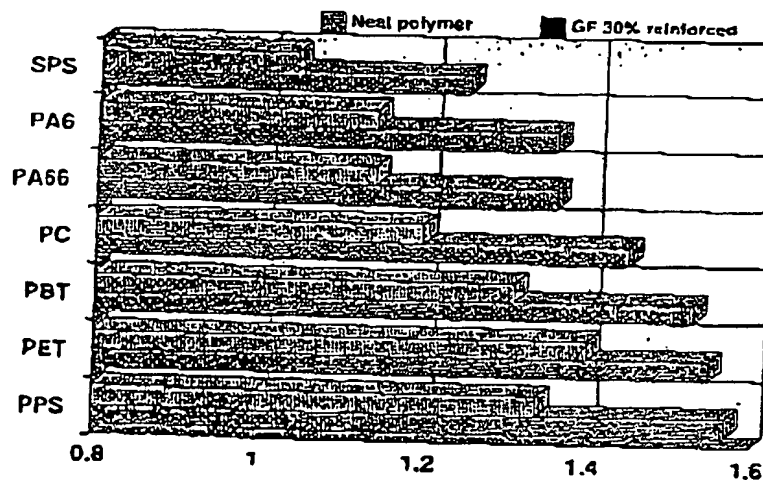
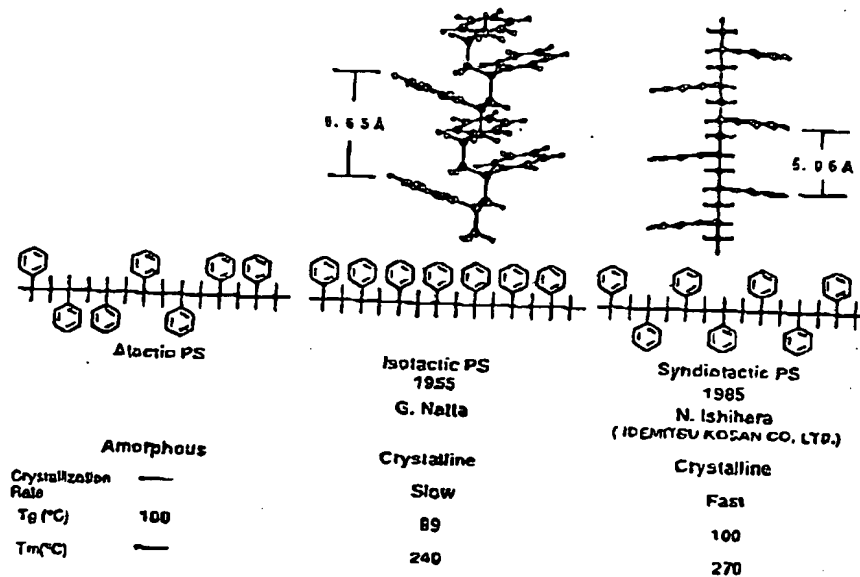


Fig. 2 DENSITY COMPARISON

its high load heat distortion temperature of 250 °C, and can be used for structural materials for harsh environment service and surface-mounting electronic components. SPS surpasses other engineering resins with a higher break down strength and lower dielectric dissipation, and is therefore expected to find widespread application in microwave devices. Furthermore, the specific gravity advantage ( approx. 25% ) of SPS over other engineering resins is worth noting ( Fig. 2, 3, 4 ).

Due to the hydrolytic stability of SPS, it usually requires no preliminary drying before processing. Compared with other crystalline engineering thermoplastics, it exhibits lower moisture uptake and less shrinkage, and a higher degree of dimensional accuracy and stability when moulded ( Fig. 5 ).

Because of the excellent properties as described above, SPS is considered to be quite useful in the field of automotive, electric and electronic applications.

### Synthesis of SPS

#### (1) Homogeneous Catalyst

As the catalyst for syndiotactic polymerization of styrene, Titanium compounds with MAO is excellent. Titanium metallocene complexes with one cyclopentadienyl ligand yield the highest activity for SPS. The substituents on their cyclopentadienyl ligand which are electron donor groups generally yield higher polymerization activities. This result suggests stabilization of active site by electron releasing substituents. The cationic nature of Group IVB metal active centers for olefin polymerization has been proposed in recent publications 4). Zr compounds were also found to catalyze syndiotactic polystyrene. In comparison with the titanium compounds, the zirconium compounds show lower activity and lower stereoregularity, which could arise from the less electrophilic and the larger ionic radius of zirconium in comparison with titanium.

The activity of the  $Cp^*TiCl_3$  is higher than the unsubstituted cyclopentadienyl complex. SPS molecular weight can be controlled primarily by temperature via  $\beta$ -hydride elimination as the chain transfer mechanism. A decrease in the molecular weight of the SPS produced with  $CpTiCl_3$  is observed relative to that for  $Cp^*TiCl_3$ . This would indicate that  $\beta$ -hydride elimination occurs more readily for  $CpTiCl_3$ .

#### (2) Heterogeneous Catalyst

Heterogeneous titanium compounds such as  $TiCl_3$ , Ti supported on Mg compound were used as a catalyst 5). When these catalysts were used, polymers having a mixture of highly isotactic and highly syndiotactic were mainly obtained (Table 1). In general, the amount of syndiotactic polystyrene increases with increasing a molar ratio of Al to Ti. Fig. 6 shows a typical  $^{13}C$ -NMR spectra of the polystyrene obtained by heterogeneous catalyst system. This single peak shows highly isotactic sequence and this single peak shows highly syndiotactic sequence. No peak between these two peaks

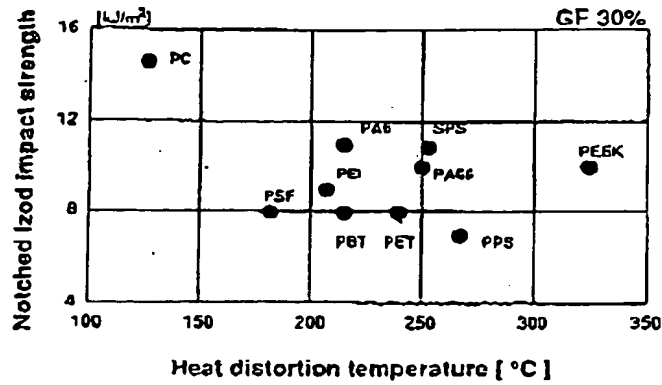


Fig. 3 Heat distortion temperature vs Notched Izod impact strength

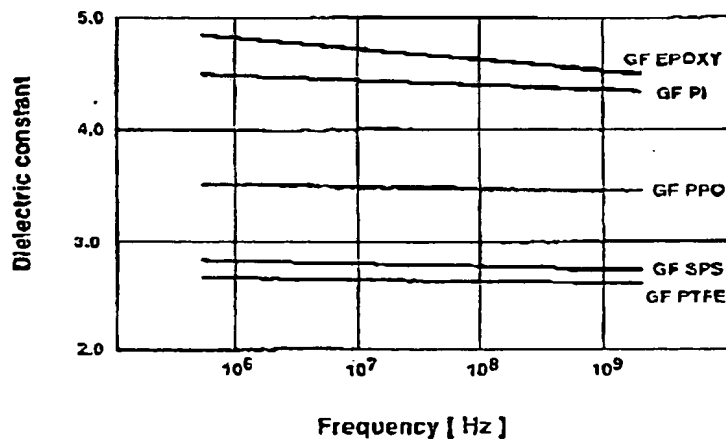


Fig. 4 DIELECTRIC CONSTANT OF GF - SPS

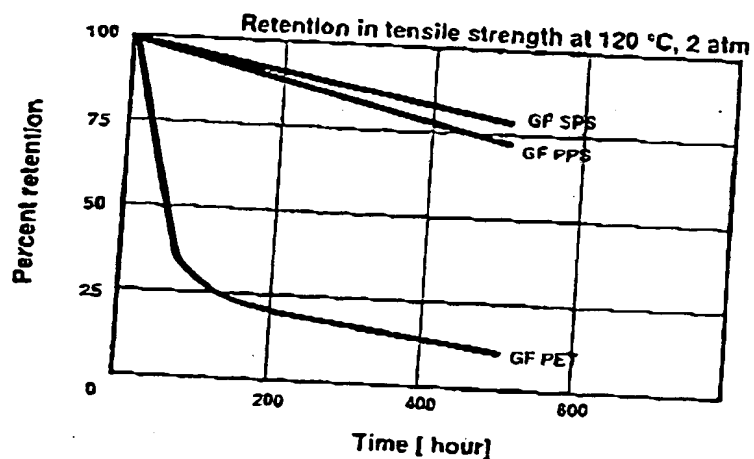


Fig. 5 WATER - VAPOUR RESISTANCE OF GF - SPS

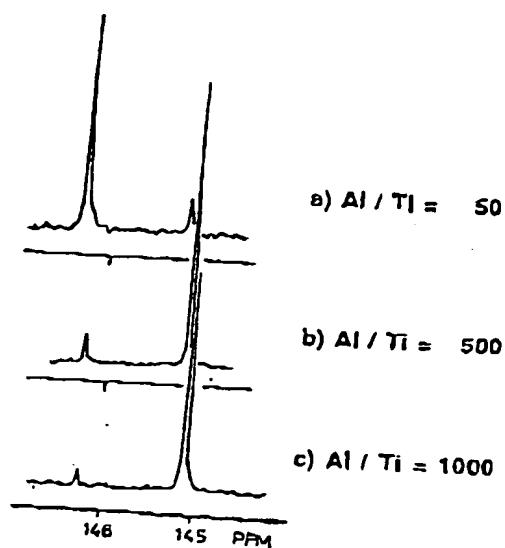


Fig. 6 Aromatic  $^{13}\text{C}$  carbon spectra of polystyrenes obtained with Mg supported  $\text{TiCl}_4$  / Malex catalyst in 1,2,4-trichlorobenzene at 130 °C with a JNMGX-270 spectrometer (at 67.8 MHz)

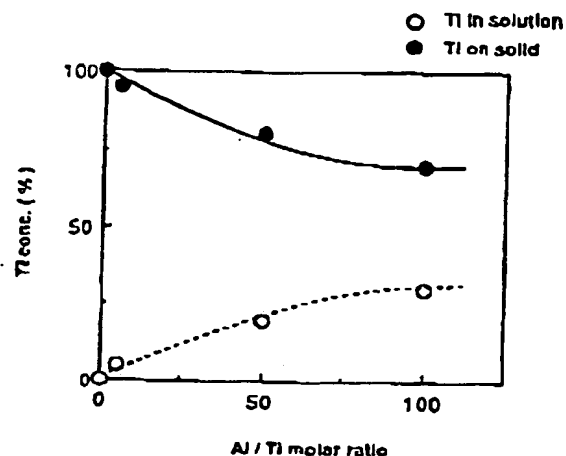


Fig. 7 Effect of Al / Ti molar ratio on Ti concentration in the solution and on the solid

Tab. 1 Polymerization of styrene using various Ti compounds with MAO

Catalyst mmol	[Al]/[Ti]		Conversion wt%	Stereospecificity
TiCl <sub>3</sub> (AA)	1.0	100	8.2	Iso.PS + Synd.PS
	0.2	1000	2.0	Iso.PS + Synd.PS
TiCl <sub>3</sub> (solvay)	1.0	20	1.9	Iso.PS + Synd.PS
	0.2	1000	0.9	Iso.PS + Synd.PS
Mg(OEt) <sub>2</sub> /EB/TiCl <sub>4</sub>	2.0	50	2.9	Iso.PS(64)+ Synd.PS(16)
	0.2	500	1.1	Iso.PS(12)+ Synd.PS(88)
	0.2	1000	1.4	Iso.PS(10)+ Synd.PS(90)
TiCl <sub>4</sub>	40	10	7.2	Iso.PS
	5	40	0.4	Iso.PS + Synd.PS
	0.2	500	0.7	Synd.PS
Yl(OEt) <sub>3</sub>	2	10	0.3	(Atactic PS)
	2	50	2.5	Synd.PS
	0.2	500	0.9	Synd.PS

a) [styrene]=0.43 mol, toluene=100 ml, 50 °C, 2hr.

indicates the absence of APS. There would be two types of polymer arising from two different active sites. In order to clarify this problem, some experiments are carried out. MAO was reacted with Ti supported on Mg compounds in toluene for about 30 minutes at room temperature and then the suspension was filtered to separate the solution from the solid phase. The solid phase was washed with n-heptane. Styrene was polymerized using both the solution part and the solid part. Isotactic polystyrene was obtained from the solid part and syndiotactic polystyrene was obtained from the solution part. These results indicate that a part of Ti on the carrier was migrated in solution on reaction with MAO, to give a soluble catalytic species that polymerizes styrene to SPS. The amount of Ti that goes into solution depends on the amount of MAO.

Heterogeneous catalyst with halogen gives polymers involved isotactic component. The amount is dependent on the Al to Ti ratio. On the other hand, homogeneous catalyst without halogen does not give isotactic polymer.

Furthermore, the titanium concentration of the solid and the solution were investigated. The results are given in this Fig. 7. The titanium concentration in solution increased with increasing the molar ratio of Al to Ti. It is suggested that the amount of Ti on the carrier that goes into solution depends on the molar ratio of Al to Ti.

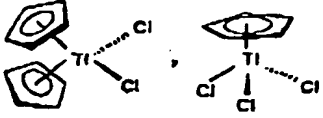




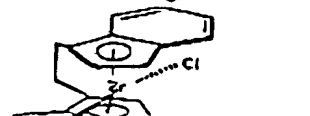
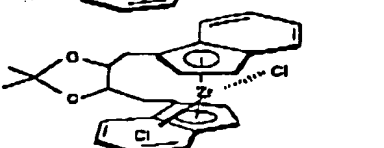
The effect of a molar ratio of MAO to Ti on the activity in the case of  $\text{CpTiCl}_3$  and MAO catalyst system was investigated. The activity increases with increasing of the molar ratio of MAO to Ti. The amount of  $\text{Ti}^{3+}$  species measured by ESR increases with increasing of the ratio of MAO to Ti, too. This suggests that MAO acts as reducing agent from  $\text{Ti}^{4+}$  to  $\text{Ti}^{3+}$ .  $\text{Ti}^{3+}$  might be a active species for synthesis of SPS. MAO acts as a weak reducing agent. Therefore, much amount of MAO is needed to increase the activity. The addition of triisobutylaluminum to  $\text{CpTiCl}_3$  / MAO catalyst was investigated. As a result, it was found that the addition of TIBA increases the activity. However, excess addition of TIBA decreased the activity.

The stereochemistry of styrene insertion into the carbon-metal bond of the catalyst has been investigated<sup>6)</sup>. The regiochemistry of insertion can in principle proceed in by a secondary process. From the investigation of deuterated polymer, it was concluded that the double-bond opening mechanism in syndiotactic polymerization was cis opening<sup>7,8)</sup>.

### (3) Ansa-metallocene Catalyst

These new ansa metallocenes have been applied to polymerization of styrene. Table 2 shows the relationships between the catalyst and stereoregularity of polymer. These titanocenes produced both atactic polypropylene and syndiotactic polystyrene. These chiral metallocenes produced both isotactic polypropylene and atactic polystyrene. However, this titanocene could produce marvelously both the

Table 2 Relationships between the catalysts and the stereoregularities of the polypropylene and polystyrene products

Catalysts	Stereoregularity	
	PP	PS
	Atactic	Syndiotactic [mm] = 1.0
	Atactic	Syndiotactic [mm] = 1.0
	Isotactic [mm] = 0.57	Syndiotactic [mm] = 1.0
	Atactic [mm] = 0.19	Atactic
	Isotactic [mm] = 0.52	Atactic
	Isotactic	Atactic
	Isotactic [m] = 0.96	Atactic

stereoregular polymers which isotactic polypropylene and syndiotactic polystyrene. This is the first example that two different stereoregular polymers can be obtained using the same catalyst.

As describe before, in syndiotactic polymerization of styrene the secondary insertion occurred. On the other hand, in isotactic polymerization of propylene the primary insertion occurred. Two different types of insertion could occur in the same catalyst. From these results, The mechanism of syndiospecific polymerization of styrene should be different from that of isospecific polymerization of olefin.

### Conclusion

The economic implications of SPS are simply stated, the polymer is based on styrene monomer. In other words, one of the distinguishing features of SPS is that the resin, which has properties comparable with those of engineering thermoplastics, is expected to bridge the current price / performance gap between commodity and specialty, depending on the market growth which provides economies of scale. For this reason, SPS will no doubt find, not just niche opportunities, but important roles in engineering applications.

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